Solid-Phase Extraction of 35 DBPs with Analysis by GC/ECD and GC/MS

Russell Chinn,[1] Tiffany Lee,[1] Stuart Krasner,[1] Melissa Dale,[1]
Susan Richardson,[2] Jonathan Pressman,[3] Tom Speth,[3]
Richard Miltner,[3] and Jane Ellen Simmons[4]
[1]Metropolitan Water District of Southern California, La Verne, CA
[2]National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens, GA
[3]National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH
[4]Experimental Toxicology Division, NHEERL/ORD, U.S. Environmental Protection Agency, Research Triangle Park, NC

ABSTRACT

An analytical method for 35 disinfection by-products (DBPs) was developed for a U.S. Environmental Protection Agency (EPA) health effects study. A toxicological evaluation was conducted on drinking water that was "scaled-up" using reverse osmosis (RO) by concentrating the total organic carbon (TOC) from a treated surface water by ~130-fold, adjusting the bromide concentration to re-establish the natural TOC to bromide ratio, and subjecting the concentrate to chlorination, using a similar chlorine dose to TOC ratio as would be used in conventional treatment. This concentrated water presented analytical challenges, which were resolved by merging two methods, which provided excellent quality control data while increasing the efficiency of the analysis and offering confirmation data for 19 of the target analytes. An automated solid phase extraction procedure was used for all of the sample preparation and the liquid-liquid extraction method was eliminated. The sample extract was divided into two separate volumes for analysis by two different instruments. The previously used liquid-liquid extraction method offered better extraction recoveries; however other drawbacks resulted in using the solid phase extraction method. Quality control data was compared between the two instrumental methods and were found to be similar. Disinfection by-product degradation was shown to occur in two ways: base catalyzed hydrolysis in water and by thermal losses during heated injections on the gas chromatograph. Analytical conditions were chosen to minimize these problems.

INTRODUCTION

The U.S.Environmental Protection Agency (EPA) has developed and undertaken a research project integrating toxicological and chemical evaluation of environmentally realistic complex mixtures of drinking water DBPs (1). The Metropolitan Water District of Southern California's Water Quality Laboratory (MWD) was selected as one of the contract laboratories to support the analytical needs of the research project referred to as the "Four Lab Study" because it was designed and is being conducted by scientists from four national laboratories of the U.S. Environmental Protection Agency's Office of Research and

Development with the assistance of extramural partners (1). MWD was responsible for the analysis of 23 out of a list of 46 analytes and a subcontract laboratory was responsible for the analysis of the other 23 analytes. MWD also provided data for 12 additional (EPA's Information Collection Rule) analytes since these compounds are included in MWD's normal monitoring program and were amendable to the analytical methods used. Analytes were chosen based on previous occurrence and toxicity work in determining emerging contaminants in drinking water (2,3,4). The listed DBPs were formed by the batch chlorination of a concentrated environmental matrix and each batch was analyzed over several days.

A multidisciplinary team was used to perform the various tasks of engineering, toxicology, data processing, chemistry, chemical analysis, and risk assessment (5,6). Because the studies proposed in the research plan involved steps that were logical but difficult to implement, a phased series of experiments was planned and implemented (1). Results from the first and second phases provided information used to guide and refine the experimental plans for the third phase the full study. The analytic methods described here were developed for the analysis of DBPs in the full study being conducted here *which has in vivo* reproductive/developmental toxicology as the priority endpoint (6).

A nationwide occurrence study (7) of a broad suite of DBPs used two analytical methods, a micro liquid-liquid extraction (MLLE) with gas chromatography/electron capture detection (GC/ECD), and solid-phase extraction (SPE) with GC/mass spectrometry (MS). Due to the complex sample matrix in this study, attempts to use conventional MLLE produced thick layers of emulsions that made the separation of a clean solvent layer very difficult. The analysis was labor-intensive and produced low analyte recoveries. However, sample preparation by SPE using a styrene divinylbenzene polymer cartridge proved successful. An automated SPE system was used for all sample preparations. GC/ECD offered some sensitivity advantages and added additional quality control over the use of GC electron impact ion trap MS; therefore the SPE extracts were split into two separate vials and both types of instruments were used for sample analyses over a seven-month period.

The 35 analytes (Table 1) included 12 Information Collection Rule (ICR) compounds and 23 non-ICR compounds. The 12 ICR compounds were the 4 regulated trihalomethanes (THMs), 4 haloacetonitriles, 2 haloketones, chloral hydrate, and chloropicrin. The 23 non-ICR compounds included 6 iodinated THMs, 4 additional haloacetonitriles, 6 additional haloacetaldehydes (HAs), and 7 additional halonitromethanes. Ascorbic acid was used to quench residual chlorine, however 5 of the compounds used ammonium chloride (AC) as a quenching agent, because some of those analytes were not stable in the presence of ascorbic acid. Therefore, duplicate samples were taken using the two different preservatives. The 5 AC compounds are less stable and were analyzed only by GC/ECD using lower temperature conditions.

Table 1: 35 Disinfection By-Product Target Analyte List and Preservatives

	Iodo-trihalomethanes(iTHM)	Acronym	Preservative
1	Dichloroiodomethane	DCIM	Ascorbic Acid
2	Bromochloroiodomethane	BCIM	Ascorbic Acid
3	Dibromoiodomethane	DBIM	Ascorbic Acid
4	Chlorodiiodomethane	CDIM	Ascorbic Acid
5	Bromodiiodomethane	BDIM	Ascorbic Acid
6	Iodoform	TIM	Ascorbic Acid
	Haloacetonitriles(HAN)		
7	Chloroacetonitrile	CAN	Ascorbic Acid
8	Bromoacetonitrile	BAN	Ascorbic Acid
9	Bromodichloroacetonitrile	BDCAN	Ammonium Chloride
10	Tribromoacetonitrile	TBAN	Ammonium Chloride
	Haloacetaldehydes(HA)		
11	Dichloroacetaldehyde	DCA	Ascorbic Acid
12	Bromochloroacetaldehyde	BCA	Ascorbic Acid
13	Dibromoacetaldehyde	DBA	Ascorbic Acid
14	Bromodichloroacetaldehyde	BDCA	Ascorbic Acid
15	Dibromochloroacetaldehyde	DBCA	Ascorbic Acid
16	Tribromoacetaldehyde	TBA	Ascorbic Acid
	Halonitromethanes(HNM)		
17	Bromonitromethane	BNM	Ascorbic Acid
18	Dichloronitromethane	DCNM	Ascorbic Acid
19	Bromochloronitromethane	BCNM	Ascorbic Acid
20	Dibromonitromethane	DBNM	Ascorbic Acid
21	Bromodichloronitromethane	BDCNM	Ammonium Chloride
22	Dibromochloronitromethane	DBCNM	Ammonium Chloride
23	Tribromonitromethane	TBNM	Ammonium Chloride
	ICR Analytes		
24	Chloroform	TCM	Ascorbic Acid
25	Bromodichloromethane	BDCM	Ascorbic Acid
26	Dibromochloromethane	DBCM	Ascorbic Acid
27	Bromoform	TBM	Ascorbic Acid
28	Dichloroacetonitrile	DCAN	Ascorbic Acid
29	Bromochloroacetonitrile	BCAN	Ascorbic Acid
30	Dibromoacetonitrile	DBAN	Ascorbic Acid
31	Trichloroacetonitrile	TCAN	Ascorbic Acid
32	Chloral Hydrate	TCA	Ascorbic Acid
33	Chloropicrin	TBNM	Ascorbic Acid
34	1,1-dichloropropane	11DCP	Ascorbic Acid
35	1,1,1-trichloropropane	111TCP	Ascorbic Acid

EXPERIMENTAL METHODS

Reagents Used

The solvent used for all extraction work and standard preparation was methyl-tertiary-butyl ether - MtBE (Omnisolve grade EMD Gibbstown, NJ). The dechlorinating agents used for sample collection were ammonium chloride (A.C.S. granular reagent, J.T. Baker, Phillipsburg, NJ) and L-ascorbic acid (A.C.S. reagent, , J.T. Baker, Phillipsburg, NJ). Reagent water used in the preparation of calibration standards and extracted sample method blanks were prepared from Milli-Q plus UV ultra-pure water (Millipore Corp., Bedford, MA).

Stock Standards

Water sampling vials containing ammonium chloride (AC) powder was used to preserve the 5 analytes listed in Table 2. Four of the compounds were obtained from a Canadian company (Orchid Cellmark, New Westminster, BC, Canada) and bromopicrin was custom synthesized by a specialty chemical company (Columbia Organic Chemical Co., Camden, SC).

Table 2: 5-Component Ammonium Chloride Analyte Spiking Solution Preparation

15 ppm 5-Component Acetonitrile Solution Preparation for the Ammonium Chloride Analytes				
#	Compound Name	Vendor Name	Stock Conc (mg/L)	CH3CN uL in 1mL	Conc (mg/L)
1	Bromodichloracetonitrile	Orchid Cellmark	2730	5.5	15.0
2	Tribromoacetonitrile	"	5902	2.55	15.1
3	Bromodichloronitromethane	"	5300	2.85	15.1
4	Dibromochloronitromethane	"	8000	1.9	15.2
5	Bromopicrin	Columbia	7500	2	15.0

Water sampling vials containing ascorbic acid (AA) powder was used to preserve the 30 analytes listed in Table 3. Fifteen of the analytes: 5 iodinated THM's, 4 halonitromethanes, and 6 haloacetaldehydes were obtained from a Canadian company (Orchid Cellmark, New Westminster, B.C. Canada).

Certified Standard Solutions

Table 3 shows the preparation of a 30 component solution prepared in acetonitrile used in preparing calibration standards and used in quality control matrix spike addition. The 12 ICR compounds were purchased as certified standard solutions. The trihalomethanes (THM) mix was a methanol solution containing all four THMs each at 2000 mg/L (Supelco, Bellefonte, PA). An EPA method 551b mix contained 7 analytes in an acetone solution each at 2000 mg/L (Supelco, Bellefonte, PA). Chloral hydrate was obtained in a methanol solution

Table 3: 30-Component Ascorbic Acid Analyte Spiking Solution Preparation

	40 ppm 30-Component AA Solution Prepared in Acetonitrile				
	Compound - acronym	Stock(1) solvent	Conc. (ug/ml)	uL in 5 ml(2)	Vendor
	THM Mix (4)				
1	Chloroform - TCM	MeOH	2000		Supelco
2	Bromodichloromethane-BDCM	MeOH	"	100.0	
3	Dibromochloromethane-DBCM	MeOH	"		
4	Bromoform - TBM	MeOH	"		
	551B Mix (7)				
5	Dichloroacetonitrile-DCAN	Acetone	2000		Supelco
6	Bromochloroacetonitrile-BCAN	Acetone	"		
7	Dibromoacetonitrile-DBAN	Acetone	"		
8	Trichloroacetonitrile-TCAN	Acetone	"	100.0	
9	1,1-Dichloropropanone-11DCP	Acetone	"		
10	1,1,1-Trichloropropanone-111TCP	Acetone	"		
11	Chloropicrin - TCNM	Acetone	"		
	Iodomethanes (6)				
12	Dichloroiodomethane - DCIM	CH3CN	5000	40.0	Orchid Cellmark
13	Bromochloroiodomethane - BCIM	CH3CN	5000	40.0	
14	Dibromoiodomethane - DBIM	CH3CN	5235	38.0	
15	Chlorodiiodomethane - CDIM	CH3CN	5000	40.0	
16	Bromodiiodomethane (s) - BDIM	CH3CN	5000	40.0	
17	Iodoform (s) - TIM	CH3CN	5000	40.0	Mallinckrodt
	Haloacetonitriles (2)				
18	Chloroacetonitrile - CAN	CH3CN	5000	40.0	Aldrich
19	Bromoacetonitrile - BAN	CH3CN	5000	40.0	
	Halonitromethanes (4)				
20	Bromonitromethane - BNM	CH3CN	5000	40.0	Orchid Cellmark
21	Dichloronitromethane - DCNM	CH3CN	5000	40.0	
22	Bromochloronitromethane - BCNM	CH3CN	5000	40.0	
23	Dibromonitromethane - DBNM	CH3CN	5000	40.0	
	Haloacetaldehydes (7)				
24	Dichloroacetaldehyde (s) - DCA	CH3CN	5000	40.0	Orchid Cellmark
25	Bromochloroacetaldehyde-BCA	CH3CN	5000	40.0	
26	Dibromoacetaldehyde - DBA	CH3CN	5000	40.0	
27	Bromodichloroacetaldehyde-BDCA	CH3CN	5000	40.0	
28	Dibromochloroacetaldehyde-DBCA	CH3CN	5000	40.0	
29	Tribromoacetaldehyde - TBA	CH3CN	5000	40.0	
30	Trichloroacetaldehyde - TCA	MeOH	1000	200.0	Supelco

(1) MeOH-methanol, CH3CN-acetonitrile, (2) prepared in acetonitrile.

at 1000 mg/L (Supelco, Bellefonte, PA). It is recommended preparing all solutions in acetonitrile since compounds have been observed to be less stable in methanol.

SAMPLE PREPARATION METHODS

Liquid-Liquid Extraction Method

A liquid-liquid extraction method used previously was also used for the stability study (7). Briefly, it used 30 ml of sample acidified to pH 3.5 then extracted by adding 10 g of sodium sulfate, 1 g copper sulfate and 3 ml of MtBE, and mechanical shaking for 23 minutes. The top ether layer is decanted and transferred to an autosampler vial and placed on the instrument for analysis.

Solid-Phase Extraction Method

The SPE method uses an automated sample preparation instrument including a dual 402-syringe pump fitted with a 25 ml and 5 ml syringe (Gilson Xli, 735 sampler software v5.2, Middleton, WI) which will allow 20 samples to be processed sequentially in one batch (8). The SPE cartridge contained 125-micrometer diameter styrene divinyl benzene polymeric beads (Varian Bond; Elut-PPL, 200mg, 3mL, Palo Alto, CA). Samples were prepared in 40 ml clear glass vials (Qorpak, Bridgeville, PA) by wrapping the top of each sample vial with aluminum foil and sealing the edges with a rubber band. The elution tube was a 12 mm diameter and 75 mm length disposable culture tube (Alltech, Deerfield, IL), and from the culture tube the MtBE extract was automatically transferred to a 2-ml amber vial with a split silicone/PTFE septum cap (Alltech, Deerfield, IL).

Table 4: Automated Solid Phase Extraction Steps

Steps	Dispense Liquid	Liquid Volume (ml)	Dispense Rate (ml/min)	Aspirate Rate (ml/min)	Pump Method	Air Push Volume (ml)	Air Push Rate (ml/min)
Condition	Methanol	8	10		Using_syringe	0	6
Load	Sample	18	5	5	Using_syringe	0	6
Load	Sample	18	5	5	Using_syringe	0	6
Elute	MtBE	1.6	1	1	Using_syringe	2	10
Extract Transfer	Aspirate Flow Rate (ml/min)	Mode	Extra Volume (uL)	Aspirate Height (mm)	Result Name	Volume (uL)	Extra Volume (uL)
	1	Liquid	0	0	Storage vials	1000	0

The SPE cartridge was first conditioned with methanol and then two sample aliquots of 18 ml each are loaded onto the cartridge since there was a volume limit on the syringe pump (Table 4). The sample was then eluted with MtBE into the culture tube and automatically transferred to a 2 ml autosampler vial. Between samples that contain high analyte levels, a rinsing method can be used

before the next sample, which will rinse the syringe pump and associated PTFE tubing with 36 ml of methanol.

Since the autosampler vial has a split septum the extracts are prone to evaporation loss so the extract was manually transferred on the same day, as analysis, to an autosampler vial and securely sealed with a solid silicone/PTFE septum cap. The extracts were stored at -19^{O}C for at least 1 hour and when used for analysis the MtBE extract is transferred to a 100-uL autosampler vial insert (Alltech, Deerfield, IL) which was then placed into a 2 ml autosampler vial.

INSTRUMENTATION

Gas Chromatograph/Electron Capture Detector

The GC was equipped with two ECD's and a model 8200 autosampler (Varian CP-3800 Analytical Associates, Inc., Walnut Creek, Calif.). There were two analytical columns installed in the GC oven: a DB-1, 30-meter, 0.25-mm i.d. narrow-bore column with a 1-µm film thickness (Phenomenex, Torrance, Calif.) and a DB-5, 30-meter, 0.25-mm i.d. narrow-bore column with a 1-µm film thickness (Phenomenex, Torrance, Calif.).

The GC used a 1079 injector with electronic flow control and a narrow bore (2 mm internal diameter) deactivated liner (Varian Analytical Associates, Inc., Walnut Creek, Calif.). After the splitless injection the split was opened after 0.77 min to a split ratio of 19:1 and then after 2.97 min the split ratio was set to 7:1. The carrier gas was helium, set to a constant flow rate of 1.7 mL/min. The autosampler was set to inject 1.9 ul of sample extract at 0.7 ul/sec using a solvent plug of 0.2 ul of MtBE.

A temperature program was used to maximize resolution of all analytes between both columns. The GC oven temperature program was as follows: isothermal column temperature at 35ºC, hold for 31 min; increase column temperature to 103ºC at a rate of 4ºC/min, with no hold time; then finally increase column oven temperature to 292ºC at 27ºC/min, and hold for 2 min. Total run time was 57.0 minutes. The ECD was set at a temperature of 303°C at range 10 with a fast time constant and capillary cell current. The make-up gas was nitrogen set to 23 ml/min. Figure 1 shows a typical chromatogram for a 20 ug/l extracted calibration standard on both columns.

Both columns shared the same 1079 injector using a one-hole 0.8 mm graphite ferrule for installation (Alltech, Deerfield, IL). A simultaneous collection of both ECD signals were collected and analyzed on a Precision 360 workstation personal computer (Dell Corp. Round Rock, TX) with XP pro service pack 1 operating system (Microsoft Corp. Redmond, WA). The chromatography software (Chromelian version 6.5, Dionex Corp., Sunnyvale, CA) was configured under a licensed server/client which allowed file processing at the office desktop. The GC/ECD method was used to analyze for 20 AA analytes that included chloral

hydrate and chloropicrin and the 5 AC analytes for a total of 25 GC analytes. The other 10 ICR analytes were not analyzed by GC/ECD to reduce the complexity of the analysis due to coelution problems. BCIM was usually not

Figure 1: Simultaneous Injection of 30 Ascorbic Acid Analytes Each at 20 ug/L on a DB-1 and DB-5 Column by GC/ECD.

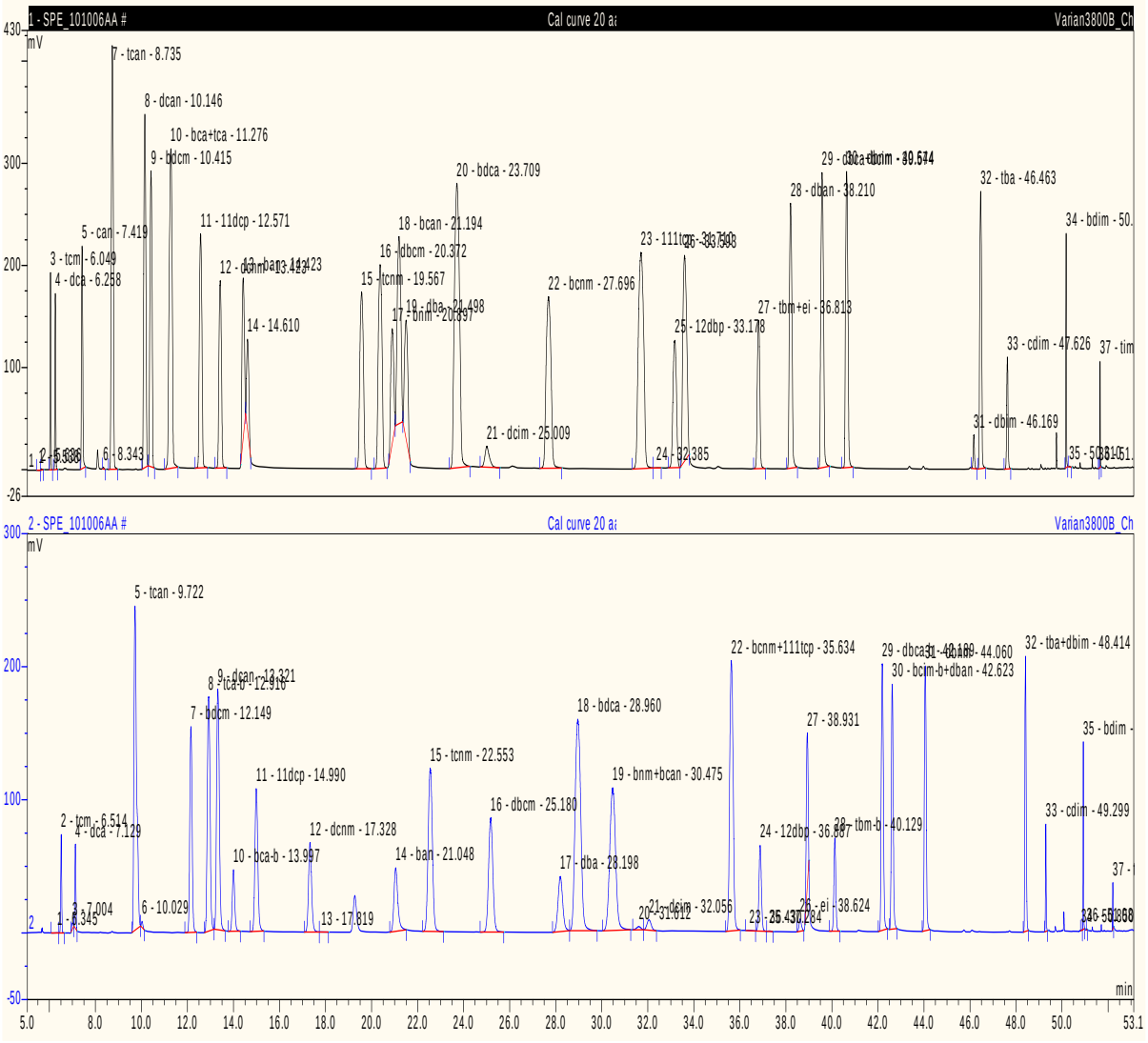


Table 5: Analyte Peak Coelutions on GC/ECD Analysis

#	DB-1 (7 coelutions)	DB-5 (6 coelutions)	AC-Fraction
1	CAN, TCAN	**CAN+TCAN**	
2	**CNM+BCA+TCA**	TCA, BCA	
3	11DCP	**CNM+11DCP**	
4	**TCNM+BDCAN**	TCNM, BDCAN	BDCAN
5	BNM, BCAN	**BNM,BCAN**	
6	**DBAN+BDCNM**	DBAN, BDCNM	BDCNM

Coeluting peaks in bold, CNM-chloronitromethane.

reported by GC/ECD due to coelution problems so a total of 19 AA analytes were reported by GC/ECD. Table 5 shows known peak coelutions on each column with a previously studied compound (7). There were a total of 13 coeluting peaks, 7 coelutions on the DB-1 column and 6 coelutions on the DB-5 column. Analyzing the AC compounds on a separate extraction helped in reducing the complexity of the GC/ECD analysis.

Gas Chromatograph/Mass Spectrometer

The instrument used was a Finnigan PolarisQ bench top ion trap MS with a Finnigan Trace 2000 Ultra GC on the MS inlet and operated by Xcaliber software (Thermo Electron Corp., Waltham, MA). GC injections were done by a CTC A200S autosampler (Leap Technologies, Carrboro, NC). The analytical column installed in the GC oven was a Rtx-1, 30-meter, 0.25-mm i.d. narrow-bore column with a 1-µm film thickness (Restek, Bellefonte, PA). The MS conditions were as follows: source temperature at 220^{o}C, damping gas 2 ml/min, maximum ion time 25, full scan mode at 40-400 amu, positive polarity, and transfer line temperature at 300^{o}C.

The GC used an injector with electronic flow control and a narrow bore (1 mm internal diameter) liner (Restek, Bellefonte, PA) for splitless injection. After the splitless injection the split was opened after 0.5 min to a split ratio of 20:1. The carrier gas was helium set at 1.2 mL/min. The injection sample volume was 3 ul. The injection temperature was set at 90^{o}C.

The GS/MS used a similar temperature program as the GC/ECD method. The GC oven temperature program is as follows: isothermal column temperature at 35ºC, hold for 23 min; increase column temperature to 139ºC at a rate of 4ºC/min, with no hold time; then finally increase column oven temperature to 301ºC at 27ºC/min, and hold for 1 min. Total run time was 56.0 minutes.

ANALYTE STABILITY

Water Sample Preservatives

It has been shown previously that most of the analytes in Table 1 can be preserved with AA when added at a concentration of 35 mg/L (9). Some of the haloacetaldydes were not previously tested in water, so additional kinetic stability testing of these compounds was performed. Five of the compounds listed in Table 3 were preserved with AC added at a concentration of 100 mg/L; therefore separate water sampling vials containing the AA and AC preservative were collected for each water sample taken. The water samples were acidified at the time of sampling with 1 molar sulfuric acid to a pH between 3 and 4 to prevent base catalyzed hydrolysis. Indicating strips for pH were used in the field to adjust the pH to the proper range. Sampling vials were prepared using AA and AC powders; solutions are not used since the preservatives can degrade when used as water solutions.

Haloacetaldehyde Stability in Water at pH 3.5

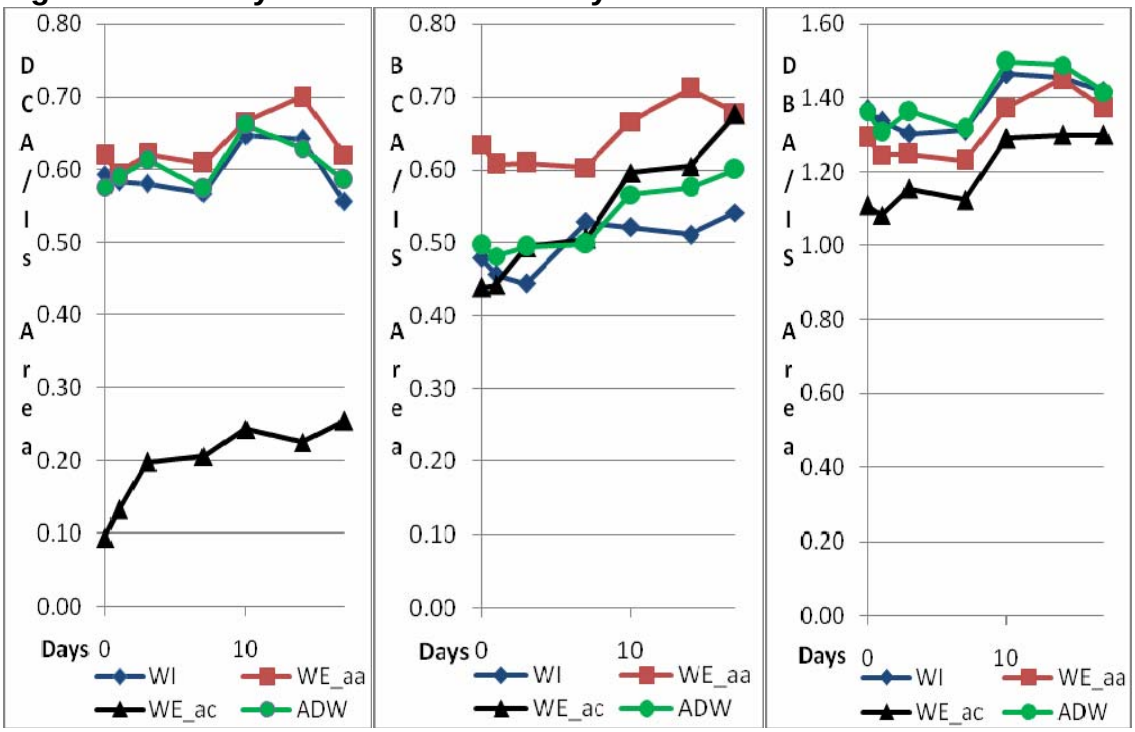
Holding studies were conducted for six HA's, not including the ICR compound chloral hydrate, to determine their stability in a water sample (Table 6). It was found that the 6 HAs were stable for over two weeks when using sulfuric acid to adjust the sample pH to 3.5 and using ascorbic acid as the chlorine quenching agent. The stability test was conducted using four different water matrix types.

Table 6: Stability Test of 6 Haloacetaldehydes in 4 Different Water Types

#	Test Type	1 (3-component DHA mix) DCA (ug/L)	DBA (ug/L)	BCA (ug/L)	2 BDCA (ug/L)	3 DBCA (ug/L)	4 TBA (ug/L)
1	WI3.5	30	30	30	30	30	30
2	WE3.5AA	30	30	30	30	30	30
3	WE3.5AC	30	30	30	30	30	30
4	ADW	30	30	30	30	30	30

WI3.5-Weymouth plant influent at pH 3.5
WE3.5AA-Weymouth plant effluent at pH 3.5 with ascorbic acid
WE3.5AC-Weymouth plant effluent at pH 3.5 with ammonium chloride
ADW-acidified distilled water at pH 3.5
DHA - dihaloacetaldehyde

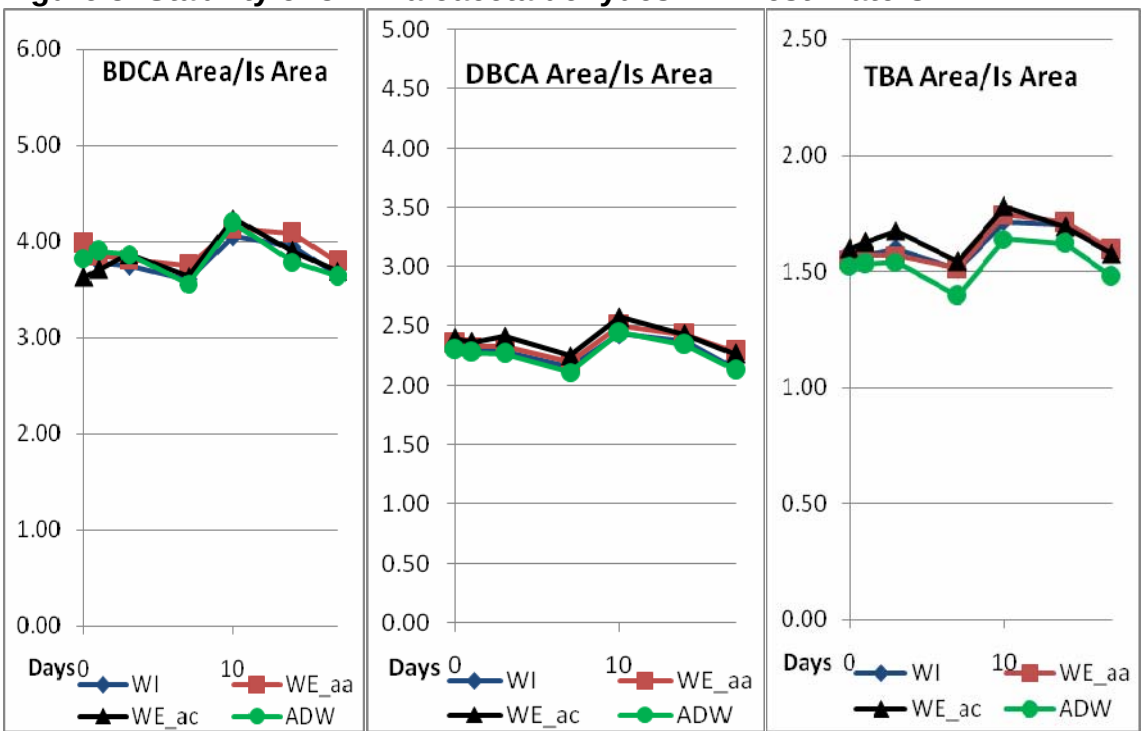
Figure 2: Stability of 3 Dihaloacetaldehydes in 4 Test Waters.



WI-Weymouth Plant Influent, La Verne, California at pH 3.5
WE_AA-Chloraminated Weymouth Plant Effluent preserved with ascorbic acid at pH 3.5
WE_AC- Chloraminated Weymouth Plant Effluent preserved with ammonium chloride at pH 3.5
ADW-acidified distilled water at pH 3.5

The first was MWD's Weymouth plant influent water of La Verne, CA, which was a blend of Colorado River water and California State Project Water, which are both surface water sources with typical total dissolved solids of 400-500 mg/L, total organic carbon of 2-3 mg/L and bromide levels of about 0.1 mg/L. The Weymouth plant effluent water is processed through chlorination, flocculation, sedimentation, filtration and then chloramination via ammonia addition prior to distribution. Two different chlorine quenching agents - ammonium chloride and ascorbic acid - were added to the Weymouth effluent water, resulting in matrices 2 and 3. Lastly distilled water was used as the fourth test water type. All of the waters were adjusted to pH 3.5 with sulfuric acid, followed by addition of the appropriate type of haloacetaldehyde solution.

Figure 3: Stability of 3 Trihaloacetaldehydes in 4 Test Waters



WI-Weymouth Plant Influent, La Verne, California at pH 3.5
WE_AA-Chloraminated Weymouth Plant Effluent preserved with ascorbic acid at pH 3.5
WE_AC-Chloraminated Weymouth Plant Effluent preserved with ammonium chloride at pH 3.5
ADW-acidified distilled water at pH 3.5

The waters were all prepared in large batches and then poured into 40-ml sampling vials. All of the sample vials were stored at 4°C throughout the test period. Each sample type was extracted in triplicate over a 17 day period. The sample holding times were day 0, day 1, day 3, day 7, day 10, day 14, and day 17. A total of 336 liquid-liquid extractions were performed and analyzed with GC/ECD.

The three dihaloacetaldehyes tested were stable in each matrix type with one exception: dichloroacetaldehyde (DCA) in Weymouth effluent with ammonium chloride had degraded by over 80% even on test day 0 (Figure 2). Ammonium chloride will form chloramines with any free chlorine residual in the sample. In

Figure 2 DCA has a slight formation increase over time in the Weymouth effluent water containing ammonium chloride. It is notable that chloral hydrate has shown a 50% loss when ammonium chloride is used as a sample collection preservative (10). All three trihaloacetaldehydes were stable in all four test waters for more than a two week period (Figure 3).

Haloacetaldehyde Stability in Water at pH 8.3

The haloacetaldehydes were shown to be adequately stable when the sample was immediately acidified in the field; however the kinetic degradation of these compounds at higher pH and their degradation by-products are shown in Table 7. The individual haloacetaldehydes were spiked into pH 8.3 distilled water and then extracted after 95 minutes. They were analyzed by GC/ECD using the LLE extraction method which is faster than the SPE method. The SPE method analyzes each sample sequentially whereas the LLE method allows extraction of all the samples in one batch at the same time. The third column in Table 7 shows the rapid and almost complete decomposition of all six compounds except for DCA. Because of the rapid decomposition of these compounds it is imperative to acidify the sample in the field without delay. The haloacetaldehydes did not form the same decomposition by-products as in the thermal degradation testing. The trihaloacetaldehydes degraded to the corresponding THMs and two of the dihaloacetaldehydes also formed THM compounds. The trihaloacetaldehydes degraded to form significant amounts of THMs in the range of 20 to 92 percent, where TCA degraded almost completely into TCM. The base hydrolysis degradation of these compounds could contribute to reporting erroneously high THM results when attempting to sample and measure for THMs, especially if no sample acidification is used.

Table 7: Base Catalyzed Hydrolysis of Haloacetaldehydes.

	Analyte initial conc 1 ppm	**% loss in 95 min @pH8.3**	**TCM** Amt (ug/L)	**BDCM** Amt (ug/L)	**DBCM** Amt (ug/L)	**TBM** Amt (ug/L)
1	**DCA**	17.4	n.a.	n.a.	n.a.	n.a.
2	**DBA**	99.5	n.a.	n.a.	n.a.	28.0
3	**BCA**	99.5	n.a.	1.3	10.2	n.a.
4	**DBCA**	99.9	n.a.	n.a.	228.0	18.0
5	**BDCA**	99.9	n.a.	201.0	8.0	n.a.
6	**TBA**	99.9	n.a.	n.a.	n.a.	237.0
7	**TCA**	99.9	917.0	n.a.	n.a.	n.a.

(1)Individual haloacetaldehydes extracted after 95 min in pH 8.3 water.

Analyte Stability at Different Injector Temperatures

It has been demonstrated which chemical is suitable as a chlorine quenching agent for which analytes, and that acidic conditions will prevent base-catalyzed hydrolysis of the analytes; however it has not been shown if all of these target

Table 8: Area Response Comparison of Individual DBPs Analyzed at Two Injection Port Temperatures 87°C Versus 261°C on a DB-1 Column by GC/ECD.

Individual AA-Analytes (Areas)				Thermal Degradation By-Product (Areas)				
Analyte	Inject Temp		%(3)		Inject Temp		Conc.	%
1ppm dir(1)	87°C	261°C	Loss	Analyte	87°C	261°C	ppb(2)	Formed
DCA	1968	1742	**11.5**					
BCA	2238	1855	**17.1**					
TBA	2445	1688	**31.0(5)**	dba	96.9	869	**96.1**	9.6
DBA	4240	3616	**14.7**					
BDCA	6271	5109	**18.5**	dca	144	387	**222.2**	22.2
DBCA	3562	2674	**24.9**	bca	47	416	**224.3**	22.4
TCNM	3228	892	**72.4(50)**	tcm	3.8	343	**350.0**	35
				dcnm	2.5	15.8	**5.7**	0.6
DCNM	3236	2748	**15.1**					
BCNM	4015	3296	**17.9**					
DBNM	2789	2392	**14.2**	bnm	24.7	320	**88.2**	8.8
BCIM	218	154	**29.4**					
DCIM	391	261	**33.2**					
DBIM	308	191	**38.0**					
CDIM	552	460	**16.7**					
BDIM	523	474	**9.4**					
TIM	26.4	40.9	**-54.9**	unk	11	185		
					6.7	97.5		

Individual AC-Analytes				Thermal Degradation By-Product				
Analyte	Inject Temp		%		Inject Temp		Conc.	%
1ppm dir(1)	87°C	261°C	Loss	Analyte	87°C	261°C	ppb(2)	Formed
BDCAN	4367	3059	**30.0**	dcan	83	175	**62.0**	6.2
BDCNM	2251	526	**76.6(50)**	bdcm	0	1388	**303.7**	30.4
TBAN	2346	1286	**45.2(5)**	dban	38	223	**86.0**	8.6
DBCNM	1591	324	**79.6(50)**	dbcm	0	1467	**274.3**	27.4
TBNM	650	93	**85.7(30)**	tbm	143	502	**224.4**	22.4
				dbnm	128	621	**259.6**	26

(1) dir-direct standards are not extracted and are prepared directly in MtBE.
(2) concentration is based on area response at 261°C.
(3) Chen et. al. previously reported degradation injected at 250°C GC/MS (12).

analytes are thermally labile. The issue of thermal stability is important in GC analysis since vaporization in the injection port normally occurs at elevated temperatures. Tests were conducted at low and high injector temperatures to determine the effect of temperature on the detection and quantitation on each target analyte. Previously, studies on bromopicrin have shown GC analysis at high injection temperatures caused it to degrade into bromoform, which is one of the regulated trihalomethanes (11). Further studies on bromopicrin and other brominated DBPs have identified other types of interferences being formed in the presence of different solvent types and when using high MS transfer line temperatures (12).

Table 8 shows selected individual analytes injected at 87^{o}C versus 261^{o}C on the DB-1 column with the same oven temperature program and settings as described above for the GC instrument. All analytes in Table 8 were prepared at 1 mg/L in MtBE. The solutions were set up to be analyzed sequentially, first at 87^{o}C then at 261^{o}C; therefore the analytical conditions were chosen to minimize differences in the analysis between the two tests runs. The U. S. compliance method for the analysis of the ICR compounds is EPA method 551.1 and it prescribes a final column temperature of 260^{o}C for 30 minutes; therefore this temperature is what these compounds are exposed to when using the EPA method (7).

Four of the AA analytes (CAN, BAN, BNM, and TIM) did not show any decrease in area response at the higher injection temperature. The other 14 AA analytes had on average a 24% decrease in area response with a range of 9-72% loss in response at the higher injection temperature. The highest degradation, 72% was seen with chloropicrin; the lowest degradation was for BDIM at 9%. Two sizable artifact peaks were found when TIM was injected at the higher injection temperature; however they have not been identified.

Some of the target analytes are actually produced when analyzed at the higher injection temperature. The right side of Table 8 shows the thermal degradation by-products produced at the 261^{o}C injection port. Six of the AA-target analytes injected at 261^{o}C produced target analyte by-products. The most significant and highest by-product produced was chloroform when chloropicrin is analyzed at the higher injection temperature.

The bottom of Table 8 shows the 5 AC-analytes, which tend to degrade to a greater extent than the AA-analytes. The AC-analytes all showed degradation losses at the higher injection temperature with an average loss of 63%. The range of degradation was 30-86%; the highest degradation was for bromopicrin at 86%, and the lowest was BDCAN at 30%. The two trihaloacetonitriles BDCAN and TBAN both lost one of their bromine atoms and produced the corresponding dihaloacetonitrile, DCAN and DBAN, respectively. The other three AC compounds are trihalonitromethanes, and each of these compounds lost their nitro group to form the corresponding THM. The AC compound that produced the highest amount of by-product was BDCNM which formed about 30% BDCM.

Chen et. al. previously reported similar degradation for seven of the trihalogenated compounds and are shown in parenthesis in Table 8 (12).

METHOD COMPARISONS

Comparison of SPE Versus LLE Extraction Methods

A comparison of the SPE and the LLE sample preparation methods was done on the GC/ECD. Standards were prepared at the 10 ug/l concentration and then extracted by the SPE method and the LLE method. Both extracts were analyzed on the GC/ECD and the area responses were compared. No calibration or quantitation was done, so true response data are compared and not processed data that would further manipulate or skew the data set. The SPE method had a

Table 9: Comparison of SPE Versus LLE Extraction Methods (AA area counts)

	TCM	DCA	CAN	BDCM	TCA	BCA	DCNM	BAN
SPE	9	31	241	6	166	59	275	1081
2.4xLLE	10	97	259	5	248	127	281	846
%SPE/LLE	**88**	**32**	**93**	**113**	**67**	**47**	**98**	**128**
	TCNM	DBCM	BNM	DBA	BDCA	DCIM	BCNM	TBM
SPE	409	13	728	255	458	59	827	7
2.4xLLE	441	16	677	674	577	72	678	12
%SPE/LLE	**93**	**84**	**108**	**38**	**79**	**83**	**122**	**56**
	DBNM	DBCA	BCIM	CDIM	DBIM	TBA	BDIM	TIM
SPE	518	326	31	102	23	402	134	127
2.4xLLE	450	425	37	113	41	393	140	167
%SPE/LLE	**115**	**77**	**84**	**90**	**56**	**102**	**96**	**76**

SPE – SPE concentration factor is 24x's.
2.4xLLE – LLE concentration factor is 10x's multiplied times 2.4.

24 times concentration factor and the LLE had a 10 times concentration factor so the area data for the LLE has been normalized to the SPE data by multiplying the area counts 2.4 times. Table 9 shows the side-by-side comparison data of both sample preparation methods. The SPE area divided by the LLE area in percent is calculated for each analyte. Normally the GC/ECD in this study quantitated 20 compounds, but six more are shown in Table 9: the 4 THMs, chloropicrin, and chloral hydrate. The overall average for the 24 compounds shown is 84%; therefore the SPE method had about 16% less absolute recovery than the LLE method. The SPE method has noticeably less extraction efficiency for the dihaloacetaldehydes where the lowest recovery ratio was for DCA at 32%. The percent response ratio for DBA and BCA was 38% and 47%, respectively.

Similarly, a comparison between the SPE and LLE extraction methods are shown for the 5 AC analytes using GC/ECD analysis in Table 10. A 10 ug/l standard was extracted by both methods and the LLE area counts are multiplied by 2.4 to normalize the concentration factors. The average percent ratio of area response between SPE and LLE was 78%; therefore the SPE method had about 22% less

recoveries on average than the LLE extraction method. The lowest recovery ratio was for BDCAN which is the only haloacetonitrile AC analyte, while the other 4 AC analytes are trihalonitromethanes which had better response ratios with a range of 74-101%. The AA analytes had an 84% average ratio and similarly the AC analytes was 78%, therefore the overall SPE extraction efficiency was about 19% less than the LLE method for all 29 compounds.
The above SPE versus LLE extraction comparison compares normalized data to show which extraction method has better absolute recoveries. Even though the LLE method had better overall extraction recoveries than the SPE method when comparing the normalized data, the SPE method still has over two times the concentration factor and can produce twice the response than the LLE extracts not accounting for the 19% less extraction efficiency for the SPE method. Other advantages of the SPE method are: it uses less solvent, it eliminated the emulsion problems in the LLE method, it is automated and saves labor costs.

Table 10: Comparison of SPE Versus LLE Extraction Methods (AC area counts)

	BDCAN	**BDCNM**	**DBCNM**	**TBNM**	**TBNM**
SPE 10 STD	312	223	162	346	64
LLE 10 STD (x2.4)	812	266	160	465	71
%SPE/LLE	**38.4**	**83.8**	**101.3**	**74.4**	**90.1**

Comparison of GC/MS and GC/ECD Quality Control

The precision and accuracy can be compared directly between the GC/ECD and GC/MS since the exact same sample extracts were split and analyzed by both instruments. Table 11 shows the 19 analytes analyzed by GC/ECD and the average percent relative difference calculated between duplicate sample extractions. Duplicates were analyzed on a ten times diluted RO sample and the count column shows the number of samples used in calculating the average for each analyte. Blanks denote that no analyte was found except for TCA which was over the calibration range. The accuracy was measured by a adding a matrix spike to a ten times diluted sample. Diluted samples were used for quality control since the undiluted sample was not amendable to matrix spike additions due to high background levels of interferences. Because of the difficult matrix the GC/ECD had some false positive problems even with two column confirmation. Interferences were more pronounced for the late eluting compounds, for example, TIM the last eluted compound.

Generally, considering the difficult sample matrix the quality control was very good for both instruments. The overall average percent relative difference for both the GC/ECD and GC/MS was 6%, so both instruments had similar precision. The average percent matrix spike recoveries for the GC/ECD and GC/MS were both 100% so both instruments had good accuracy. However, the average standard deviation for the GC/ECD and GC/MS duplicates was 6% and 8% respectively. The average standard deviation between the GC/ECD and

GC/MS for the matrix spike recoveries was 15% and 19%, respectively. Overall the GC/MS had slightly better accuracy and precision over the GC/ECD quality control results.

Table 11: Accuracy and Precision Between GC/ECD and GC/MS

Analyte	GC/MS						GC/ECD				
	dup			spk (n=16)			dup			spk (n=15)	
	% rel difference			% Recoveries			% rel difference			% Recoveries	
	avg	stdev	count	avg	stdev		avg	stdev	count	avg	stdev
iTHM											
DCIM				103.9	13.3					103.2	13.8
DBIM				98.9	14.8					102.1	24.7
CDIM				101.5	13.7					105.4	19.8
BDIM				103.0	15.1					84.2	14.2
TIM				106.6	16.8		4.3	37.4	4.0	114.2	27.3
HAN											
CAN	7.3	9.2	3.0	97.5	11.8		4.3	4.5	6.0	88.9	21.3
BAN	4.7	4.2	3.0	102.4	10.3		9.3	6.2	8.0	117.5	19.6
HA											
DCA	7.3	5.3	23.0	84.9	23.3		7.9	6.6	23.0	72.5	30.0
BCA	7.5	5.6	23.0	89.8	14.7		10.4	7.6	23.0	96.9	22.8
DBA	5.5	4.8	13.0	90.5	11.6		6.9	4.7	12.0	97.2	21.2
TCA											
BDCA	3.9	2.9	24.0	92.1	15.0		4.6	5.0	24.0	86.3	15.4
DBCA	5.4	5.4	23.0	100.2	15.7		4.4	4.1	24.0	103.1	14.4
TBA				102.4	13.9					97.1	14.1
HNM											
BNM				102.9	11.5					111.6	31.1
DCNM	9.3	12.2	7.0	103.0	15.4		2.9	2.1	10.0	107.9	13.2
BCNM				104.9	15.3					106.5	12.4
DBNM				105.2	15.6					105.2	14.4
TCNM	5.7	5.1	24.0	97.6	15.7		2.9	2.3	25.0	99.1	14.9

Dup-duplicate, spk-matrix spike addition, avg-average, stdev-standard deviation.

Comparison of GC/MS and GC/ECD Sensitivities

The instrument sensitivities can be compared directly since the sample preparation was exactly the same for each instrument. The exact same SPE extract was divided into separate autosampler vials and injected on the GC/MS and the GC/ECD. An overall comparison of the reporting limits for each method is given in Table 12. Basically, the GC/MS had slightly higher reporting limits

for some of the compounds than the GC/ECD. The overall sensitivity varied with sample matrix issues and instrument operation. Table 12 has some representative reporting limits (RL) used in data processing and reporting. Generally, the GC/MS and the GC/ECD gave similar sensitivity overall depending on the sample matrix, as well as the instrument condition.

Table 12: Comparison of Reporting Limits Between GC/MS and GC/ECD

Name	GC/MS RL(ug/L)	GC/ECD RL(ug/L)
Halomethanes		
TCM - Chloroform	1	
BDCM	1	
DBCM	1	
TBM - Bromoform	1-2.5	
DCIM	1-2.5	1
BCIM	1-2.5	1
DBIM	1	1
CDIM	1	1
BDIM	1-2.5	1
TIM - Iodoform	1-5	1
Haloacetonitriles		
CAN	1	1
BAN	1-2.5	1
DCAN	1-2.5	
BCAN	1	
DBAN	1	
TCAN	2.5	

Name	GC/MS RL(ug/L)	GC/ECD RL(ug/L)
Haloketones		
1,1-DCP	1-5	
1,1,1-TCP	1-5	
Haloacetaldehydes		
DCA	1-2.5	1
BCA	1-2.5	1
DBA	1	1
TCA	1	1
BDCA	1-2.5	1
DBCA	1	1
TBA	1-2.5	1
Halonitromethanes		
BNM	1-2.5	1
DCNM	1-2.5	1
BCNM	1-2.5	1
DBNM	1	1
TCNM	2.5	1

CONCLUSION

The use of an automated SPE sample preparation procedure instead of an LLE method saved time and resources, plus produced good QC on a very difficult concentrated sample matrix. The six haloacetaldehydes stability test in water indicated that all of the haloacetaldehydes were stable for 17 days when using the ascorbic acid preservative and sample acidification to pH 3.5 with sulfuric acid. The stability testing of all the target analytes at 261^{o}C temperature indicated that the ammonium chloride analytes were more thermally labile than the ascorbic acid analytes. Trihalogenated compounds have been known to be thermally less stable and when using a high injection temperature and in addition, six of the dihalogenated compounds were also found to be susceptible to thermal losses. When analyzing for trihalomethanes at high injection temperatures or during the heating process in purge and trap analysis may lead to the breakdown of trihalonitromethane compounds into their corresponding THMs, which could be a source of reporting inflated levels of THM data. Another problem that can occur is when adding these compounds as matrix spike quality control components may cause elevated THM recoveries. Additionally, using pH 8.3 sampling conditions can cause rapid and almost complete degradation of five

haloacetaldehydes producing significant amounts of THM as by-products. Two very important areas to consider when attempting DBP analysis is the careful control of thermal analytical conditions and pH adjustment at the time of sampling. If the proper analysis temperature and pH control is not used then a higher amount of THM or DBP may be reported erroneously.

Comparison between the SPE and LLE extraction efficiencies indicated that the SPE method had less extraction efficiency than the LLE method, especially for the dihaloacetaldehyde analytes. The instrument sensitivities between the GC/MS and GC/ECD were similar depending on the sample matrix and instrument operation. The accuracy and precision for the two instruments were very similar and the GC/MS produced slightly less scatter when comparing the average standard deviations for the target analyte list. Further studies are needed to complete this report regarding the use of pH 5.5 as prescribed in EPA method 551.1 where some DBPs may degrade into THMs or other target analytes that may cause a shift in the reported DBP's.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

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